

A COMPARISON OF METHODS FOR THE
DETERMINATION OF THE AREA OF
MOLECULES IN ADSORBED
SOLUBLE FILMS

A DISSERTATION
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

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GUILFORD L. MACK
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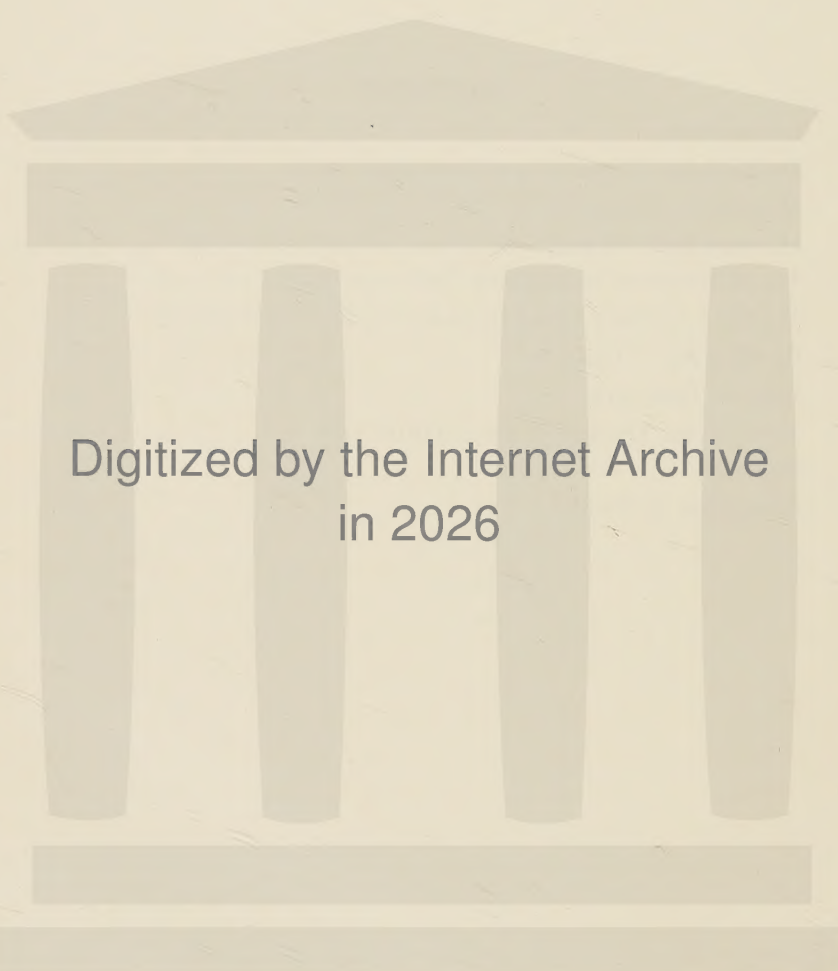
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A COMPARISON OF METHODS FOR THE DETERMINATION OF THE AREA OF ADSORBED MOLECULES IN INTERFACIAL FILMS

Introduction

The problem of determining the dimensions of an individual molecule is one that has received considerable attention. There are in general two widely different methods available for attacking this problem. One method is that employed for calculating the dimensions of the molecule from the x-ray diffraction pattern of crystals. This has heretofore been limited in application to solids possessing a crystalline structure. Recently, however, Stewart¹ by means of refined methods of measurement, has applied this method to liquids. The other principal method of attack is from the standpoint of surface chemistry. The thickness of films may be determined and calculations may be made from molecular volume data for the area of the molecule.

Surface films are of two types, namely: those formed by insoluble highly adsorbed substances and those formed by soluble and less strongly adsorbed substances. The former may be investigated by measurement of so-called surface pressures and the latter by measurement of surface or interfacial tension. Calculations of molecular area by this latter method have been accomplished (a) by the limiting slope method of Langmuir² or by the similar maximum adsorption method as used by Harkins and Wampler³ and (b) by application of the mixture law method of Mathews and Stamm.⁴

In the present research interfacial tension measurements of water against binary organic liquid systems were made. Calculations of molecular area were carried out by, (a) maximum adsorption method, (b) the mixture law method, and (c) a modified mixture law method.

Methods for Calculation of Molecular Area

The methods above mentioned for the determination of the areas of molecules in soluble films entail the determination of interfacial tension values with which, by means of the Gibbs formulation, $q = - \frac{1}{RT} \frac{dS_{23}}{d \ln c}$, the areas can be

¹ Chem. Rev., **6**, 483 (1929).

² J. Am. Chem. Soc., **39**, 1848 (1917).

³ J. Am. Chem. Soc., **53**, 850 (1931).

⁴ J. Am. Chem. Soc., **46**, 1071, 2880 (1924).

calculated. In this formulation q represents the mols adsorbed per square cm., and S_{23} the interfacial tension in dynes per cm; the other symbols have their usual significance. Mathews and Stamm have obtained interfacial tension data and have made use of both the limiting slope method and the mixture law method. The agreement of the values thus calculated was only fair.

Maximum Adsorption. The maximum adsorption method is based upon the principle first pointed out by Langmuir, that when the slope of the S_{23} , $\ln c$ curve becomes constant, q (the amount of solute adsorbed) is at its maximum value and is independent of concentration. This maximum value of q , which we shall represent as q_L is supposed to represent the number of molecules necessary to form a completely saturated surface layer of adsorbed molecules. Since q_L is expressed in mols/cm², $1/Nq_L$ (N = Avogadro number) gives the number of square cm. per molecule, or the effective area occupied by the individual molecule.

Mixture Law Method. The mixture law as related to surface tension has generally been stated, in effect, as follows: the surface tension of a binary solution is a linear function of the concentration. Mathews and Stamm considered that the law would be equally applicable to the similar interfacial tension relationships and assumed further that the interfacial tension value of a binary solution against water is a linear function of the concentration in the interfacial layer.

The mixture law method of Mathews and Stamm involves the use of the interfacial tension-concentration graph and is dependent on the validity of the mixture law. If on this graph a straight line is drawn between the interfacial tension values of the two pure constituents, this line is assumed to represent the concentration of the interfacial film of the mixtures at the corresponding interfacial tension values. The horizontal distance between a point on this line and the corresponding point on the determined interfacial tension-concentration curve is assumed to give a measure of the excess concentration at the interface. This gives, then, the excess surface concentration in mols/cm³. From the Gibbs adsorption equation, the number of mols adsorbed per square centimeter of surface may be calculated. Dividing the latter number by the former gives the thickness of the surface film in centimeters. The dimensions of this equation are:

$$\frac{\text{mols} \times \text{cm}^{-2}}{\text{mols} \times \text{cm}^{-3}} = \text{cm.}$$

If the film consists of a monomolecular layer of oriented molecules, this gives directly the length of the individual molecule. Its area is calculated by means of the equation $a = M/Ndt$, in which d represents density, and t , the thickness of the film in cm. M and N have the customary significance. In carrying out the calculation it is necessary to make the further assumption that it is justifiable to apply density measurements, which are properly a function of the liquid in bulk, to discrete particles of molecular dimensions.

It should be pointed out that Langmuir had previously employed for the calculation of molecular area a special case of this method which was later

developed more generally by Mathews and Stamm. The equation for calculating the thickness of the surface layer was first given by Langmuir in the form:

$$t = q/(c' - c)$$

In this equation c' represents concentration in moles per liter at the surface, and c the concentration in moles per liter in the bulk of the solution. The surface tension values of water and ethyl alcohol are raised by the addition of soluble salts, hence these solutes must be negatively adsorbed. In other words the solvent is preferentially adsorbed, and hence, it follows that the surface layer consists of molecules of pure solvent, and the concentration of solute in the surface, c' , becomes zero. This condition then leads logically to a method for determining the area of the *solvent molecules*. In contrast to this the method applied by Mathews and Stamm gives the area of the *solute molecules*, since in their work the solute is preferentially adsorbed. Their contribution consists in the use of the mixture law to evaluate the factor c' in the above equation.

The values obtained by the so-called mixture law method are obviously dependent upon the validity of this law, while the values obtained by the maximum adsorption method are independent of the mixture law. Attention should be called to the fact that the validity of the mixture law has never been logically established, and further, it is a question whether the fractional constituents of a given mixture shall be expressed as volume fractions, as mol fractions, or as weight fractions. Mathews and Stamm justify their adoption of the mixture law on the ground that the same linear relationship has been reported by Worley¹ to hold for the similar phenomena of surface tension. They state that "for constituents of like polarity against air, which have no orienting effect, the relationship was fairly well followed, as would be expected when there was no concentrating in the interface."

Since Worley reported but one case in which the mixture law appeared to hold, general conclusions based upon his results seem questionable.

The Validity of the Mixture Law. The original formulation of the mixture law was proposed by Rodenbeck.² Other investigators have attempted to discover a relationship between surface tension and concentration of mixed liquids and the formulations proposed by them vary from the original only in the units used for expressing the concentration of the constituents. Much confusion appears to have existed on this point. Some authors have used mol fraction, others volume fraction and still others weight fraction. None of these authors has really justified the selection of units used by him. A critical and comprehensive review of the literature is given by Morgan and Griggs.³ They calculated the effect of employing the different units for a large number of systems, and found that the use of weight fraction units gave least deviation from the linear relationship.

¹ J. Chem. Soc., **105**, 267 (1914).

² Inaug. Diss., Born (1879).

³ J. Am. Chem. Soc., **39**, 2261 (1917).

They used bulk concentration values in their calculations. Since surface tension is primarily a function of surface concentration the use of bulk concentration values would not be justified in establishing a relationship between concentration and surface tension.

Application of the theoretical considerations of Gibbs¹ would show that bulk concentration and surface concentration must in fact be quite different, so that the mixture law as expressed by Morgan and Griggs would not be expected to hold. In conformity with the second law of thermodynamics it must follow that from a binary liquid system, the constituent of lowest surface tension must concentrate at the interface in order that the free surface energy will be at the lowest level possible. Differences in the dielectric moments of the molecules and differences in the internal pressures of the liquids may cut down the adsorption in certain instances, but in any case the relative molecular concentrations in the interface cannot be the same as the relative concentrations in the bulk of the solution. It is not to be expected, then, that the interfacial tension or surface tension should bear any simple relationship to the concentration in the bulk of the solution. The principal objection to the mixture law formulations, as applied to surface tension, is, therefore, that they express the interfacial tension as a function of the bulk concentration and not as a function of the interfacial concentration.

The surface tension relationships calculated by Morgan and Griggs on the basis of weight fraction were interpreted as indicating a fair agreement with the mixture law. In those cases in which one component of the binary system shows a tendency toward strong preferential adsorption a close agreement would not be expected. Those units which will, when plotted, give a marked sagging of the surface tension-concentration curve are likely more nearly correct than those which show an apparent better agreement.

Methods of Testing the Validity of the Mixture Law. A direct test of the validity of the mixture law as applied to interfacial tension relationships presents a problem of great difficulty since no method is available for the accurate measurement of the interfacial concentration. An approximate method for testing this law might be one based upon the fact that of the two methods available for calculating molecular area, one, the limiting slope method, is independent of the validity of the mixture law, while the other method is directly dependent upon it. The values of the molecular area calculated according to the Langmuir limiting slope method may, by the proper selection of components, be used as a basis for comparison of the values found from the other (thickness of film or mixture law) method. By using the different concentration units for expressing the concentration factor a comparison of the values thus obtained with those obtained by the limiting slope method should serve as a means of testing the validity of the mixture law. This should also provide an experimental basis for choosing the correct concentration units.

As has been mentioned above, if the interfacial tension of a binary mixture of liquids is plotted against the concentration of one constituent in the solution, a curve is obtained which usually sags below the straight line drawn be-

¹ "Scientific Papers," 1, 219 (1906).

tween the interfacial tension values of the two pure constituents. Only a very few cases have been reported in which the interfacial tensions of the mixtures rose above the straight line, and in each of these cases association, ionization, or other intramolecular changes not characteristic of ideal solutions are known to occur. If, in a nearly ideal solution, the interfacial tension of the mixture is greater than the value calculated from the mixture law, it would seem likely that the wrong concentration units have been used. Now if a system is selected whose constituents have similar polarities and interfacial tensions, the adsorption will be small and only slight deviations below the straight line function will be observed.

If the constituents are chosen so that the density and molecular weight ratios are widely different, use of the correct concentration units should give values conforming to the calculated interfacial tension values. If the wrong concentration units are used interfacial tension values greater than the calculated will be obtained and these units will thus be eliminated from further consideration.

Modified Mixture Law Method. It has been shown that the thickness of the surface film, t , may be determined by dividing the excess surface concentration in mols per cm^2 by the excess surface concentration in mols per cm^3 . Similarly if the total surface concentration in mols per cm^2 were divided by the total surface concentration in mols per cm^3 , this would give another method for determining the thickness of the surface film. The total interfacial concentration in mols per cm^3 is obtained directly from the mixture law and is represented, in the formulation previously discussed, by the symbol c' . The total interfacial concentration in mols per cm^2 is found from q , the increase in concentration due to adsorption, and from the concentration in the surface before adsorption occurs. This latter factor may be assumed to be equal to the $2/3$ power of the concentration in the bulk of the solution. The equation for calculating the thickness of the film may be formulated as follows:

$$t = \frac{q + c^{2/3}/N^{1/3}}{c'}$$

Where c = bulk concentration in mols/ cm^3
and c' = interfacial concentration in mols/ cm^3 .

This method of calculation has been designated as the modified mixture law method. A full explanation of this formulation will be given later.

Method for Measurement of Interfacial Tension. The methods available for the determination of interfacial tension have not been so thoroughly tested with liquid-liquid systems as they have for the corresponding liquid-air systems. The validity of the different equations used has not, in all cases, been firmly established. It is therefore not surprising that much of the interfacial tension data found in the literature is considerably in error. If adsorption at the interface occurs, only static methods are applicable. Of these methods, the sessile drop and ring methods are not sufficiently accurate for exact work. The maximum bubble pressure method has not as yet been extensively applied to interfacial tension measurements. There remain, then,

the methods involving the measurement of the drop volume or the capillary rise. The ease of operation, together with the simple and firmly established formulation for calculating the interfacial tension, led to the adoption of the capillary rise method. It was realized, however, that much more care in cleaning the apparatus and in purifying the liquids was necessary in the capillary method in order to obtain results comparable in accuracy with those obtainable with the drop volume method. On the other hand, the density of the organic liquid used need not be known so accurately as in the drop volume method. This is an important factor to consider in dealing with mixed liquids of widely differing vapor pressures.

The method of Bartell and Miller¹ was selected for use in this investigation.

During the progress of this research, it was necessary to determine the interfacial tension of water against several different liquids which were expensive and which were difficult to obtain in large quantities in the pure state. It became highly desirable to develop a method which would require but a small amount of organic liquid for each measurement.

It was found that by making use of two capillaries of different diameters an apparatus could be constructed which would give very good results and which would require not more than about 2 cc. of organic liquid. A detailed description of this apparatus will be given in another paper.

The thermostat employed was an ordinary rectangular brass box of about 15 liters capacity, fitted with plane glass sides. It was equipped with the usual heating and cooling coils. The mercury regulator held the temperature constant to within $\pm 0.03^{\circ}\text{C}$. The stirrer was equipped with a convenient switch so that it could be turned off at the moment of making a reading through the telescope of the cathetometer. The vibration of the stirring apparatus often causes such agitation of the liquid surfaces that the position of the wide meniscus cannot be accurately determined.

A 75-watt lamp mounted behind a ground glass screen was used as the source of illumination. A mirror, 2 x 18 inches, was set at an angle of 45° to a line passing through the center of the telescope. It also made an angle of 45° with the ground glass plate which was parallel to the line of sight through the telescope. This method of illuminating the wide meniscii was compared with the methods used by Richards and Coombs² and by Harkins and Humphrey.³ The results obtained were found to agree closely with those obtained by the other methods.

Purification of Liquids. One of the principal sources of error in the determination of surface tension and of interfacial tension values is the presence of capillary-active impurities in the liquids. Thus, strongly adsorbed substances need be present only in infinitesimal amounts in order to produce a marked change in interfacial tension. The capillary height method of measurement used in this work is particularly susceptible to this effect. This method

¹ J. Am. Chem. Soc., **50**, 1961 (1928).

² J. Am. Chem. Soc., **37**, 1643 (1915).

³ J. Am. Chem. Soc., **38**, 242 (1916).

is much more static than other methods, such as the drop volume or maximum bubble pressure methods, and impurities have more time to diffuse through the liquid and collect at the interface. For this reason, special care was taken in the purification of all liquids used. With one exception, namely toluene, the standards of purity attained are as high as any previously reported in the literature. The physical constants of all the liquids used had been precisely defined by one or more investigators. The following constants were selected for comparison with the best values in the literature as an indication of the purity of the compound. These values were checked within the limit of the experimental error in every case except the one previously noted.

Density. Specific gravity bottles of 25 and 50 cc. capacity with very finely ground glass joints were used in these determinations. The temperature of the measurement was determined with a thermometer certified by the U. S. Bureau of Standards and the variation was not more than $\pm 0.02^{\circ}\text{C}$. The volume of the specific gravity bottles at each temperature was determined by finding the weight of water contained and dividing by the known density of pure water at that temperature. This gives the absolute volumes reduced to 3.98°C .

The density was found in general to be the most sensitive criterion of purity. Other properties in special cases are better indicators of the presence of small amounts of impurities, but the density is the best single standard. In this connection it should be emphasized that no single physical property is a reliable measure of the chemical homogeneity of a given liquid. Unless the nature and specific effect of the impurities are known, several different and characteristic properties must be determined.

Boiling Point. The boiling points were determined with precision thermometers having a total range of fifty degrees, graduated in tenths of a degree, and calibrated by the Bureau of Standards except where otherwise noted. Every precaution necessary for obtaining the true ebullition temperature was observed and all corrections applied. All values have been reduced to a barometric pressure of 760 mm. of mercury. Where no values of dp/dt in the neighborhood of the boiling point were available, the integrated form of the Clausius-Clapeyron equation was used for the calculation. It was realized that a correct and constant boiling point is one of the least reliable tests of purity. Therefore, the closely checking results obtained for every liquid investigated were not necessarily considered to be proofs of a high degree of purity.

Freezing Points. Because many of the liquids employed in this research have very low freezing points, it was not practical to make these determinations in all cases. The values recorded agree very closely with the best of those reported by other workers, and this may be taken as a quite reliable indication of the absence of impurities.

The liquids used in addition to water were benzene, toluene, ethylbenzene, n-butylbenzene, nitrobenzene, chlorobenzene and dimethyl aniline.

The methods of purification are indicated in Tables I and II. The boiling points, freezing points and density values are given and are compared with a few of the best values from the literature.

The water used throughout these experiments was of conductivity grade. Care was taken to remove all traces of dissolved air and carbon dioxide in order to avoid any changes in density due to the presence of dissolved gases.

TABLE I

Substance	Method of Purification	Boiling Points °C		Authors
		Found	Other Values	
Benzene	Method of Richards and Shipley ¹	80.20	80.20	Young
		80.21	80.20	T. & M. (1926)
Toluene	Same as above without recrystallization	110.72 ± .01	110.7	Young
			110.6	Perkin
			110.46	R. & S. (1916)
			110.80	T. & M. (1926)
Ethylbenzene	Hg, CaCl ₂ , P ₂ O ₅ fr. two times	136.11 ± .01	136.18	Young & For- tey
			136.1	Mathews
			135.98	Richards & Barry
			136.15	T. & M. (1926)
Butylbenzene	Same as toluene	183.46 ± .10	183.10	T. & M. (1928)
			180.	Reed & Foster
Nitrobenzene	HCl, K ₂ CO ₃ , steam dist., fr., vac. fr. twice, cryst. twice	210.9 ± .1	210.8	Perkin
			209.2	Friswell
			210.60	Louguinine
Chlorobenzene	NaOH, steam dist. twice, CaCl ₂ , P ₂ O ₅ , fr.	132.01 ± .01	132.00	Young
			131.7	Mathews
			132.00	T. & M. (1926)
Dimethyl-aniline	Method of Nelson and Wales ²	194.	193	Perkin
			193.1	Kahlbaum
			192.68	Louguinine

¹ Richards and Shipley: J. Am. Chem. Soc., **38**, 989 (1916).

² Nelson and Wales: J. Am. Chem. Soc., **47**, 867 (1925).

TABLE II

Substance	Freezing Points °C		Temp.	Densities (Ref. to 3.98°C)		Author
	Found	Other Values		Found	Other Values	
Benzene	5.49 ± .01	5.58	25.13°	0.8732	0.8736	Young
	5.50 ± .01	5.50			0.87351	T. & M. (1926)
		5.493				R. C. & S.
					0.87344	Patterson
					0.87329	Int. Crit. Tab.
			20.15°	0.8783	0.8788	R. & S. (1924)
					0.8790	R. & S. (1916)
					0.8788	Young
					0.87862	Int. Crit. Tab.
					0.87879	T. & M. (1926)
Toluene			25.13°	0.8610	0.86225	T. & M. (1926)
					0.8624	Perkin
					0.8610	Int. Crit. Tab.
Ethyl- benzene			25.13°	0.8625	0.8624	Int. Crit. Tab.
					0.86239	T. & M. (1926)
Butyl- benzene			25.13°	0.8561	0.8563	T. & M. (1928)
Nitro- benzene	5.60 ± .02	5.67				Tamman
		5.7				Hansen
		5.82				Louguinine
			25.13°	1.1980	1.1972	Walden
					1.1983	Perkin
					1.1981	Int. Crit. Tab.
Chloro- benzene			15.13°	1.2078	1.2080	Int. Crit. Tab.
			25.13°	1.1008	1.1008	T. & M. (1926)
					1.1010	Perkin
Dimethyl- aniline	2.25 ± .02	2.5				Menschutkin
		1.96				Ampoula & Rimatoni
			25.13°	0.9518	0.9518	Int. Crit. Tab.

References to the Literature giving the preceding physical constants are listed below:

Ampoula and Rimatori	Gazz., 27 , 51 (1897).
Bramley	J. Chem. Soc., 109 , 454 (1916).
Friswell	J. Chem. Soc., 71 , 1010 (1897).
Hansen	Z. physik. Chem., 48 , 493 (1904).
Kahlbaum	Z. physik. Chem., 26 , 606 (1898).
Louguinine	Ann. Chim. Phys., (7) 27 , 116 (1902).
Mathews	J. Am. Chem. Soc., 48 , 562 (1926).
Menschutkin	Chem. Centr., 1898 II, 479.
Patterson	J. Chem. Soc., 81 , 1097 (1902).
Perkin (1896)	J. Chem. Soc., 69 , 1191 (1896).
Reed and Foster	J. Am. Chem. Soc., 48 , 1606 (1926).
Richards and Barry	J. Am. Chem. Soc., 37 , 998 (1915).
Richards, Carver and Schrumb	J. Am. Chem. Soc., 41 , 2019 (1919).
Richards and Shipley (1914)	J. Am. Chem. Soc., 36 , 1825 (1914).
Richards and Shipley (1916)	J. Am. Chem. Soc., 38 , 983 (1916).
Tamman	"Krystallisieren und Schmelzen," 227 (1903).
Timmermans and Martin	J. Chim. phys., 23 , 747 (1926).
	J. Chim. phys., 25 , 411 (1928).
Walden	Z. physik. Chem., 65 , 141 (1908).
Young	Sci. Proc. Roy. Dublin Soc., N. S. 12 , 374 (1910).
Young and Fortey	J. Chem. Soc., 83 , 45 (1903).
International Critical Tables, III, p. 27.	

General Procedure

The solutions of the organic liquids were made up in all cases by weight. A few of the more dilute solutions were prepared by the method of successive dilutions, but, in general all the mixtures were made up directly from the pure liquids. They were preserved in Pyrex flasks having tightly-fitting ground glass stoppers. In most cases the interfacial tensions were determined within a few days after the solutions were made up. Errors due to changes in concentration by preferential evaporation of the more volatile constituent of the mixture were thus kept at a minimum.

With the Bartell-Miller method the densities need not be determined with extreme accuracy. A reasonable amount of care is necessary, however, in order to cut down the probable error from this source to a negligible quantity. Accordingly the densities of each pure liquid and every mixture were determined in 25 cc. or 50 cc. specific gravity bottles. It is believed that these determinations are not in error by more than ± 0.0002 units.

With the double capillary method used by us the density measurements are of decidedly secondary importance. Accordingly the densities of the mixtures were calculated from the volume percent of each constituent present. The density of a mixture of approximately 50 percent composition was determined. This has been shown to represent the maximum deviation from the calculated density.¹ By interpolation the increase in density on mixing could then be determined for each mixture. These corrections very seldom caused any change in the calculated value of the interfacial tension.

Mixtures of nitrobenzene were made up with each of the four hydrocarbons, benzene, toluene, ethylbenzene and butylbenzene. The interfacial tensions of these solutions against water at 25° C were determined throughout

¹ Brown: J. Chem. Soc., **39** (1881); Linebarger: Am. Chem. J., **18**, 429 (1896).

the concentration range. The interfacial tension values of the mixtures with benzene were also determined at 15° and 35° C; those with toluene at the additional temperatures of 15°, 30° and 35° C. Mixtures of dimethyl aniline were made up with benzene, and the interfacial tension values throughout the concentration range were determined at 35° C. The values obtained at 25° are given in Tables III and IV. The final results calculated from data obtained at the other temperatures are given in Table IX.

The amount of nitrobenzene adsorbed at the interface has been calculated by means of the modified Gibbs equation, $q = -\frac{1}{RT} \frac{d S_{23}}{d \ln c}$. The adsorption from the different solvents is found to increase in the order benzene < toluene < ethylbenzene < butylbenzene; this would be expected from the relative differences between the interfacial tensions of the pure liquids. Because the solutions are so nearly "ideal" it is felt that the adsorption equation should hold reasonably well up to concentrations of fifty percent, at which concentration the maximum value of q is very nearly reached. At higher concentrations the equation obviously fails to express the true values. This will be discussed more fully in a later section.

TABLE III
Adsorption of Nitrobenzene
From Benzene Solution at 25.13°C

Concentration of Solution mols/cc $\times 10^{-3}$	Nat. Log. Concentration $\ln C-10$	Interfacial Tension dynes/cm.	Slope $\frac{d S_{23}}{d \ln c}$	Amt. Adsorbed q mols/cm ²
0.0000	—	34.70	0.000	0.0000
0.3355	2.0001	33.80	0.834	0.3364
1.0020	3.0942	32.60	1.360	0.5484
2.485	4.0025	30.67	2.80	1.129
3.877	4.4473	29.32	3.46	1.395
5.742	4.8400	27.79	4.13	1.666
7.480	5.1044	26.70	4.20	1.694
9.736	5.3680	25.73	4.20	1.694

From Toluene Solution at 25.13° C

0.0000	—	36.30	0.000	0.0000
0.2899	1.8506	35.50	0.822	0.3315
0.4718	2.3411	35.06	1.170	0.4719
0.5678	2.5263	34.06	1.410	0.5685
1.440	3.4569	33.38	2.133	0.8602
2.440	3.9686	31.86	3.668	1.479
6.120	4.9039	28.00	4.605	1.858
9.736	5.3680	25.73	4.780	1.928

TABLE IV
Adsorption of Nitrobenzene
from an Homologous Series of Hydrocarbons at
25.13° C Ethylbenzene Solution

Concentration of solution mols/cc $\times 10^{-3}$	Nat. Log. Concentration $\ln C-10$	Interfacial Tension dynes/cm.	Slope $\frac{d S_{23}}{d \ln c}$	Amt. Adsorbed q mols/cm ²
0.0000	—	38.39	0.000	0.0000
0.1974	1.4698	37.77	0.464	0.1871
0.3652	2.0850	37.18	1.440	0.5808
0.7264	2.7726	36.04	1.834	0.7396
1.807	3.6839	33.73	3.446	1.390
3.515	4.3492	31.15	4.214	1.699
5.916	4.8698	28.94	4.570	2.206
9.736	5.3680	25.73	5.918	2.387

Butyl Benzene Solution

0.0000	—	41.58	0.000	0.0000
0.1968	1.4464	40.23	0.671	0.2706
0.5252	2.4517	38.51	2.553	1.030
1.604	3.5647	35.00	3.916	1.579
3.107	4.2259	32.03	4.770	1.924
6.246	4.9241	28.48	6.135	2.474
9.736	5.3680	25.73	6.355	2.563

Tests of the Validity of the Mixture Law. For this purpose the chlorobenzene-benzene system was selected. These liquids form practically an "ideal solution"; there is no appreciable volume change or heat effect on mixing. One would expect benzene with its lower interfacial tension to be positively adsorbed. Owing to its non-polar nature, however, its preferential adsorption is small. Unfortunately for our purpose the density and molecular weight ratios are not greatly different, so that the calculated difference between the volume fraction and mol fraction of the mixture is small.

Using the mol fraction units several experimental points on the interfacial tension-concentration curve were found to fall slightly above the straight line curve. The differences are so small, however, that they could be attributed to experimental errors. When weight fraction units are used the resulting interfacial tension-concentration curve falls far below the calculated values. When volume fraction units are used a curve is obtained which is slightly below the straight line curve indicating a slight preferential adsorption of benzene as would be expected. The results of these tests are then most favorable to the use of the volume fraction units; they are not, however, to be regarded as being conclusive. Further confirmation of the correctness of these units was obtained in data presented in Table VI, the significance of which will be discussed later. It is evident, however, that the use of volume fraction units yields results which agree among themselves much better than those obtained by the use of mol fraction units.

TABLE V
Test of Validity of Mixture Law
Method of Maximum Limiting Concentration
Chlorobenzene-Benzene System at 25°C

Interfacial Tension dynes/cm.	Weight Fraction Benzene	Mol Fraction Benzene	Volume Fraction Benzene	Limit Fraction Calc. from mixture law
36.72	0.2628	0.3392	0.3099	0.378
35.98	0.5480	0.6359	0.6045	0.607
35.33	0.7577	0.8183	0.7975	0.810
34.96	0.9016	0.9296	0.9204	0.926
34.74	0.9636	0.9745	0.9709	0.992

Correction for Molecules normally present in the Surface.—Langmuir¹ and others have made calculations of molecular area by employing maximum adsorption values of q (i.e. q_L values) and substituting in the equation $a = 1/Nq_L$. These calculations have been based upon data obtained from comparatively dilute solutions.

It appears that this method should not be extended to the more concentrated solutions without taking into account the molecules of adsorbate normally present in the interface before adsorption occurs. The number of molecules thus present in one square centimeter of surface has been assumed to be equal to the two-thirds power of the number of molecules contained in one cubic centimeter of the solution. If c is expressed in mols per cm^3 then $(cN)^{2/3}$ gives the number of molecules lying in a plane of 1 cm^2 area within the solution. This term divided by N (or $c^{2/3}/N^{1/3}$) will give the number of moles per cm^2 initially present in the surface layer.

The total concentration of the interfacial layer should thus be equal to the sum $(q + c^{2/3}/N^{1/3})$.

In the dilute concentration range considered by Langmuir the factor $c^{2/3}/N^{1/3}$ is very small in comparison with q , and lies within limits of the experimental error in determining the latter value. Consequently, it need not be considered in these cases. Harkins and Wampler² have recently shown that in several cases the correction becomes appreciable at concentrations of approximately 1 mol per liter. In our work the value of $c^{2/3}/N^{1/3}$ was usually found to be one to two times greater than that of q . Mathews and Stamm made use of the limiting slope method for calculating the area of molecules adsorbed from concentrated solutions but they did not take into account the molecules initially present in the interface. It would seem that this method of calculation should give results several times too large.

An attempt was made in our work to obtain evidence bearing upon this point.

¹ J. Am. Chem. Soc., **39**, 1848 (1917).

² J. Am. Chem. Soc., **53**, 850 (1931).

TABLE VI
Molecular Area of Nitrobenzene
Adsorption from Butylbenzene Solution at 25° C.

Mol Fraction Concentration Units									
Fraction Nitrobenzene	Slope $\frac{d S_{23}}{d \ln c}$	Interface Concentration				Thickness of Film $\text{cm.} \times 10^{-7}$		Molecular Area $\text{cm}^2 \times 10^{-16}$	
		Total mols/cm ³ $\times 10^{-3}$	Excess mols/cm ³ $\times 10^{-3}$	Adsorbed mols/cm ² $\times 10^{-10}$ (a)	Total mols/cm ² $\times 10^{-10}$	cm. $\times 10^{-7}$		from Thickness	Max. Ads. (c)
						(a)	(b)		
0.0305	0.671	0.503	0.306	0.2706	0.6704	0.885	1.331	19.2 (12.7)	246.
0.0800	2.553	1.412	0.887	1.030	1.799	1.161	1.273	14.6 (13.3)	91.6
0.2313	3.916	2.878	1.274	1.579	3.198	1.339	1.111	13.7 15.3	51.6
0.4167	4.770	4.485	1.378	1.924	4.439	1.393	0.990	12.1 17.1	37.2
0.7318	6.135	7.04	0.79	2.474	6.481	3.14	0.992	18.4	30.6
1.000	6.355	9.736	—	2.563	7.949		0.817	20.8	30.6
						Average 14.9		18.4	Limit 30.6
Volume Fraction Concentration Units									
0.0202	0.671	0.808	0.611	0.2706	0.6704	0.443	0.830	26.2 (20.4)	246.
0.0540	2.553	1.889	1.364	1.030	1.799	0.755	0.952	22.4 (17.8)	91.6
0.0647	3.916	4.055	2.451	1.579	3.198	0.645	0.710	26.3 23.8	51.6
0.3190	4.770	5.865	2.758	1.924	4.439	0.608	0.758	24.3 22.4	37.2
0.6415	6.135	8.04	1.79	2.474	6.481	1.382	0.807	21.0 20.8	30.6
1.00	6.355	9.736	0.00	2.563	7.949		0.817	20.8	30.6
						Average 24.8		22.0	Limit 30.6

The amount of adsorption at the interface was determined by measurement of interfacial tension and application of the Gibbs formulation. The amount of solute present at the interface at each concentration investigated was also calculated. The sum of these theoretically give the total amount of solute at the interface.

Data obtained for a given system are given in the form of a graph in Fig. 1. While the curves shown on this graph have been plotted from actual data, no units have been given in order that the figure may be considered as being applicable to a perfectly general case.

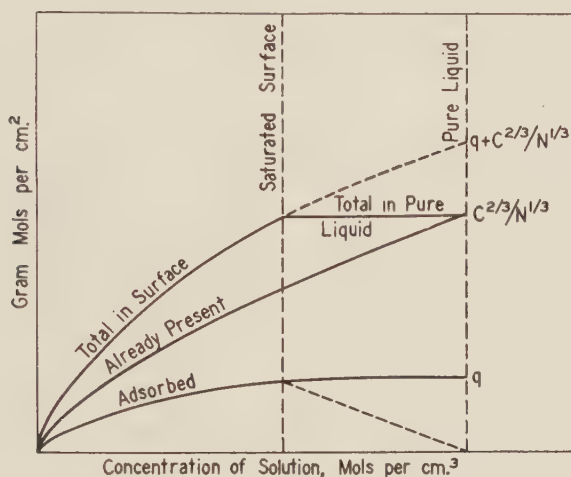


FIG. 1
Molecules of Adsorbate present at an Interface

The lower curve of Fig. 1 represents the number of mols adsorbed at the liquid-liquid interface, as calculated by means of the Gibbs equation. This equation is derived upon the necessary condition that the osmotic pressure within the solution be proportional to the mol fraction of the constituents present¹. For the nearly ideal solutions used in this work it has been assumed that this condition does hold up to a concentration of one mol per liter, and a close approximation of it may be expected to hold up to four or five times this concentration. This is about the concentration necessary for the production of a saturated surface layer of the solute molecules. In substantiation of the statement that the calculated values of q are approximately correct, it may be pointed out that q has very nearly attained its maximum value at that concentration which is in equilibrium with a saturated interface. Above this concentration the equation fails to express the true values of the adsorption. These deviations will be discussed later.

The middle curve of Fig. 1 represents the number of the solute molecules present in a unit surface assuming they are here randomly distributed as they are throughout an unit volume.

¹ Milner: Phil. Mag., (6) 13, 96 (1907).

Considering a plane in the interior of the solution it seems reasonable to expect that the number of molecules per square centimeter should be equal to the two thirds power of the molecules per cubic centimeter. If this plane be moved into the interface, the perfectly random distribution normally occurring in the bulk of the solution may be affected by the unbalanced surface forces. The solute molecules being, in general, quite polar in nature will be oriented in the interface even when no adsorption occurs. Then, unless the molecules are symmetrical in shape and uniform in all dimensions, the curve will not represent the true number of mols present in the interface.

The upper curve is given by the sum of the values of the two lower curves and represents the total number of molecules at the interface. The upper dotted portion of this curve represents imaginary values, since the surface concentration cannot exceed that found for the pure solute liquid. The calculated total number of mols in the surface is thus in error by at least the amount which is represented by the vertical distance between the dotted line and solid horizontal line representing the number of mols in a saturated surface. This error may be due to errors introduced in either or both of the component parts of the sum. By assuming the $c^{2/3}/N^{1/3}$ factor to be correct, a more probable value of q is obtained which is represented by the lower dotted line shown in the figure. This dotted line together with the first portion of the solid adsorption curve represent the maximum values of q . Ostwald and Izzaguirre¹ as well as several workers in this laboratory² have obtained results which indicate that the actual relative adsorption is practically always less than the theoretical maximum values except in the dilute solutions. They obtained an equation which appears to give the correct relative values throughout the concentration range. These corrections could not be attempted in this paper, since no method is available for the conversion of relative adsorption values to absolute values.

Summarization of Methods

In recapitulation the methods available for the determination of area of adsorbed molecules in interfacial films are as follows:

(1) Maximum adsorption method.

The maximum adsorption method as referred to in this paper is based upon the limiting slope method used by Langmuir. In case c (the concentration of solute in bulk) is not negligible in comparison to c' (the concentration of solute in the interface) the number of molecules of solute normally present in the interface before adsorption must be taken into account, the total number of molecules at the interface being represented by the formulation $q_L + c^{2/3}/N^{1/3}$. In the maximum adsorption method the total number of molecules were considered. It follows then that the limiting slope method used by Langmuir and the "maximum adsorption" method used by us differ only by the factor $c^{2/3}/N^{1/3}$ which was used in the latter method.

¹ Kolloid-Z., 30, 279 (1922); 32, 57 (1923).

² Bartell and Sloan: J. Am. Chem. Soc., 51, 1643 (1929); Bartell and Miller: Thesis (unpublished), University of Michigan (1929); Bartell and Scheffler: J. Am. Chem. Soc., 53, 2507 (1931); Bartell, Scheffler and Sloan: 53, 2501 (1931).

TABLE VII

Molecular Area of Nitrobenzene
Adsorption from Benzene Solution at 25° C

Vol. Fraction Nitro- benzene	Slope d S ₂₃ d ln c	Interface Concentration			Thickness of Film		Molecular Area	
		Total mols/cm ³ × 10 ⁻³	Excess mols/cm ³ × 10 ⁻³	Adsorbed mols/cm ² × 10 ⁻¹⁰ (a)	Total mols/cm ² × 10 ⁻¹⁰ (b)	cm. × 10 ⁻⁷ (a)	(b)	Max. Ads. (c)
0.0345	0.834	0.9975	0.6620	0.3364	0.9068	.508	.909	181.9
0.1029	1.360	2.335	1.333	0.5484	1.7314	.411	.743	95.3
0.2552	2.80	4.450	1.965	1.129	3.296	.575	.742	50.0
0.3982	3.46	5.90	2.02	1.395	4.311	.691	.731	38.2
0.5895	4.13	7.49	1.75	1.666	5.455	.952	.728	30.6
0.7683	4.20	8.68	1.20	1.694	6.213	1.412	.716	30.6
1.0000	4.20	9.736	0.00	1.694	7.080	.728	.728	30.6
						Average 34.6		
						23.2	Limit 30.6	

Adsorption from Toluene Solution at 25° C

0.0297	0.822	0.866	0.597	0.3315	0.8478	.556	.958	195.
0.0485	1.170	1.315	0.843	0.4719	1.188	.560	.904	139.
0.0583	1.410	1.529	0.961	0.5685	1.379	.591	.902	120.
0.1478	2.133	2.931	1.491	0.8602	2.367	.577	.809	70.
0.2468	3.668	4.187	1.785	1.479	3.598		.800	45.8
0.6286	4.605	7.741	1.621	1.858	5.811		.751	30.6
1.0000	4.780	9.736	0.00	1.928	7.314		.751	30.6
						Average 29.7		
						20.6	Limit 30.6	

TABLE VIII
Molecular Area of Nitrobenzene
Adsorption from Ethylbenzene Solution at 25° C

Vol. Fraction Nitro- benzene	Slope d S_{25} d ln c	Interfacial Concentration				Molecular Area				
		Total mols/cm ³ × 10 ⁻³	Excess mols/cm ³ × 10 ⁻³	Adsorbed mols/cm ² × 10 ⁻¹⁰ (a)	Total mols/cm ² × 10 ⁻¹⁰ (b)	Thickness of Film cm. × 10 ⁻⁷		From Film Thickness cm ² × 10 ⁻¹⁶ (a)	Max. Ads. (c)	
						(a)	(b)			
.02028	0.464	0.6281	0.4307	0.1871	0.5877	.435	0.936	38.9	18.1	281.
.03751	1.440	1.042	0.677	0.5808	1.184	.858	1.136	19.8	16.4	139.
.07461	1.834	1.826	1.100	0.7396	1.695	.672	0.928	25.2	18.3	97.
.1855	3.446	3.592	1.785	1.390	3.143	.779	0.875		19.4	52.5
.3609	4.214	5.569	2.054	1.699	4.430	.828	0.796		21.3	37.2
.6097	5.470	7.272	1.356	2.206	6.057	1.627	0.834		20.3	30.6
1.0000	5.918	9.736	0.00	2.387	7.773	.00	0.798		21.2	30.6
		Average 27.2				20.1		Limit 30.6		

The values of the molecular areas as calculated by this method are given by the reciprocal of the corrected total number of molecules per cm^2 in the interface. This treatment has been previously discussed in connection with Fig. 1.

(2) The mixture law method as used by Mathews and Stamm has been fully discussed and needs no further amplification at this point.

(3) The modified mixture law method has also been discussed. The difference between this method and the mixture law method is brought out by the emphasis given below.

$$\begin{aligned}
 & \begin{array}{cc} \text{Mixture Law Method} & \text{Modified Mixture Law Method} \\ \text{(a)} & \text{(b)} \end{array} \\
 t = & \frac{\text{mols adsorbed}/\text{cm}^2}{\text{mols adsorbed}/\text{cm}^3} = \frac{\text{total mols in surface}/\text{cm}^2}{\text{total mols in surface}/\text{cm}^3} \\
 = & \frac{q}{c' - c} = \frac{q + c^{2/3}/N^{1/3}}{c'}
 \end{aligned}$$

In Tables VII and VIII both of these methods have been used in calculating the molecular area of nitrobenzene, the different columns being labeled as above, (a) and (b) respectively. The third column (c) contains data obtained by the maximum adsorption method. In the same way, a number of other values of the molecular area of nitrobenzene and dimethyl aniline have been calculated. These results are summarized in Table IX.

For the purpose of comparison with the data of Mathews and Stamm a fourth column (d) is included in the table, the values of which have been calculated according to the original limiting slope method when applied to concentrated solutions. It is seen that these values are much too high.

TABLE IX
Molecular Area of Nitrobenzene and of Dimethyl Aniline
A Summary of Values

<i>Nitrobenzene</i> Solvent	Temperature	Area per Molecule $\text{cm}^2 \times 10^{-16}$			
		(a)	(b)	(c)	(d)
Benzene	15°	39.2	23.0	30.4	94.8
"	25°	34.6	23.2	30.6	97.4
"	35°	33.3	22.5	30.8	100.5
Toluene	15°	34.5	21.7	30.4	88.5
"	25°	29.7	21.5	30.6	85.7
"	30°	32.4	21.5	30.7	87.1
"	35°	33.4	20.9	30.8	87.8
Ethylbenzene	25°	27.2	20.6	30.6	69.1
Butylbenzene	25°	24.8	21.0	30.6	64.5
	Average	32.1	21.8	30.6	86.2
<i>Dimethyl Aniline</i>					
Benzene	35°	41.5	26.6	35.5	111.3
Benzene (Mathews & Stamm)	25°	38.4	—	—	75.2
Heptane (" " ")	25°	34.8	—	—	57.8

a = area calculated from mixture law method.

b = " " " modified mixture law method.

c = " " " maximum adsorption method.

d = " " " limiting slope method.

Discussion of Results

The results presented in column (a) calculated by the mixture law method are subject to the errors inherent in the modified Gibbs adsorption equation and to the errors inherent in the mixture law method as used.

The results presented in column (b) calculated by the modified mixture law method are subject to all the errors of the previous method and in addition to the error involved in the assumption that the number of molecules originally present in unit area within the bulk of the solution is the same as the number present in unit area of surface.

This method has the advantage over the original mixture law method in that the data obtained throughout the entire concentration range may be used, while the original mixture law method is limited in application to points on the first portion of the interfacial tension-concentration curve in which the maximum adsorption values have not been reached. It is in this range that the absolute values of the quantities from which the molecular areas are calculated are relatively small. Hence, the same experimental error produces a much larger relative error in the calculated value of area than would be obtained by use of the other method. At very low concentrations, low values are obtained by the second method. This may be the result of the relatively stronger tendency for the molecules near the surface to become oriented. The spatial distribution of the molecules will then be furthest from a random arrangement and the calculated value of the factor $c^{2/3}/N^{1/3}$ will be in error by a greater amount with these dilute solutions.

The results obtained in column (c) calculated by the maximum adsorption method show good agreement with the values in column (a). The reliability of the results calculated by the maximum adsorption method is subject to question. This method cannot be considered to compare in accuracy with the similar limiting slope method when this latter method is applied to dilute solutions of highly adsorbable substances. It is evident that the *final* limit value obtained by the maximum adsorption method is independent of the amount of adsorption, and depends only upon the molecular volume of the adsorbed molecules. The arbitrary manner of this calculation throws considerable doubt upon the validity of the results.

None of the methods above described for determining the area of adsorbed molecules are entirely free from theoretical objections. The values obtained and presented in this paper agree among themselves more closely than have values previously obtained by similar methods.

The methods which have so far been used in this paper for the calculation of molecular area, while widely different in many respects, are alike in that they all depend upon surface film measurements. Comparison with the values obtained by Stewart from the totally different method based upon the measurement of the diffraction of x-rays by liquids should provide a good test of the absolute accuracy of the surface film methods. At the same time it furnishes an independent check of the theory of cybotaxis upon which Stewart's calculations of molecular diameter are based. Investigations by the

x-ray diffraction method upon the particular liquids used by us are not available, but values for a sufficient number of substitution products of benzene have been worked out by Stewart to enable one to draw quite definite conclusions as to the most probable dimensions of nitrobenzene and dimethyl aniline. The values given in Table X are compatible in every case with the results presented in this paper.

TABLE X

The Area of Molecules calculated from Stewart's Values
for the Molecular Diameters

Substance	Molecular Diameter cm. $\times 10^{-8}$	Molecular Area sq. cm. $\times 10^{-16}$
Benzene	4.70	31.4
Toluene	5.06	34.8
Ethylbenzene	4.99	40.6
Isopropylbenzene	5.36	43.0
Phenol	4.77	30.8
Aniline	4.75	31.8

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